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CRYSTAL GROWTH METHOD FOR GROUP-III NITRIDE AND RELATED COMPOUND SEMICONDUCTORS

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a method for growing group-III nitrides and related compound semiconductors on a substrate consisting of, for example, sapphire and, more particularly, to a method for growing epitaxial layers of group-III nitride and related compound semiconductors by means of metalorganic chemical vapor deposition (to be referred to as MOCVD hereinafter).

2. Description of the Related Art

To realize high-efficiency, high-brightness blue and ultraviolet light-emiting diodes and lasers, group-III nitride and related compound semiconductors have been researched and developed in recent years. As a method for growing group-III nitride and related compound semiconductors, MOCVD is currently widely used.

In a typical MOCVD process, group-III nitride and related compound semiconductors are generally grown hetero-epitaxially on sapphire substrates. However, due to the large differences in lattice constant and thermal expansion coefficient between the group-III nitride and sapphire, it is really difficult to obtain high quality epitaxial layers of group-III nitride and related compound semiconductors. In order to solve this problem, several methods have been proposed in the past decade. The first one was demonstrated by Amano, et al. (U. S. Patent 4,855,249, and Appl. Phys. Lett. Vol. 48, 1986, pp. 353-355) who grew the group-III nitride and related compound semiconductors on a low-temperature grown AlN single buffer layer instead of growing them directly on the sapphire substrates. The second and now widely adopted method was proposed by Nakamura et al. (U. S. Patent 5,290,393 amd Jpn. J. Appl. Phys. Vol. 32, 1993, pp. L16-L19). According to this method, a $Ga_xAl_{1-x}N$ ($0 < x \leq 1$) single buffer layer was grown on the sapphire substrate at low temperature prior to the growth of the group-III nitride and related compound semiconductor films. More recently, a new method has been developed by Uchida et al. (Proceedings of the Second International Conference on Nitride

Semiconductors, Tokushima, Japan, 1997, pp. 214-215) and Turnbull et al. (J. Appl. Phys. Vol. 80, 1996, pp. 4609-4614). In this method, the so-called double buffer layers which consist of two GaN layers or one GaN and one AlN layer, deposited successively at two different or identical temperatures, were firstly grown on the sapphire substrate, and the group-III nitride and related compound semiconductor films were then grown on the specially designed double buffer layers.

By making use of these recently developed technologies (especially the second one), blue-light emitting diodes based on the group-III nitride and related compound semiconductors have become commercially available. However, according to these conventionally proposed methods, not only the growth conditions, such as the growth temperature for the single or double buffer layers and the thickness of the buffer layer are strictly restricted (most satisfactory result reported up to date has been achieved at a growth temperature of 450 °C and a total layer thickness of 25 nm when employing these buffers), but also the material combination is quite limited (so far only GaN and $Ga_xAl_{1-x}N$ $(0 \leq x \leq 1)$ were used as the buffer layers), which may prevent them from meeting the objectives of fabricating good quality optoelectronic devices. Therefore, the crystal growth method needs to be further improved in order to enhance the crystallinity of the group-III nitride and related compound semiconductors.

SUMMARY OF THE INVENTION

The present invention has been made in consideration of the above situation and has as one of its objectives, to provide a crystal growth method for the group-III nitride and related compound semiconductors, yielding as high a crystal quality as possible while maintaining freedom in choosing material systems for practical applications.

It is another objective of the present invention to provide a method which can grow a p- or n-type semiconductor layer with an excellent characteristic so as to allow formation of an excellent p-n junction for use in a nitride-based light-emitting device and a laser diode.

According to the present invention, there is provided a crystal growth method for the group-III nitride and related compound semiconductors, comprising of the following steps:

Forming a MOCVD-grown periodic or nonperiodic multi-layered buffer on a substrate at a first temperature, in which the layers alternate between two types of compound semiconductors A and B different from each other in lattice constant, energy band gap, layer thickness, and composition; and

Forming a MOCVD-grown layer of a group-III nitride or related compound semiconductor on the formed multi-layered buffer, at a second temperature which is higher than the first.

According to the present invention, a group-III nitride or related compound semiconductor layer can be doped n- or p-type as it is MOCVD-grown on the obtained buffer formed on a substrate.

Additional objectives and advantages of the invention will be set forth in the description which follows, and in part will be obvious from the description, or may be learned by practice of the invention. The objectives and advantages of the invention may be realized and obtained by means of the techniques and combinations thereof particularly pointed out in the appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying drawings, which are incorporated and constitute a part of the specification, illustrate presently preferred embodiments of the invention, and together with the general description given above and the detailed description of the preferred embodiments given below, serve to explain the principles of the invention.

FIG. 1 is a schematic sectional view showing a $Ga_xAl_{1-x}N$ ($0 \leq x \leq 1$) crystal grown on a conventional AlN single buffer layer on a sapphire substrate;

FIG. 2 is a schematic sectional view showing a $Ga_xAl_{1-x}N$ ($0 \leq x \leq 1$) crystal grown on a conventional $Ga_yAl_{1-y}N$ ($0 < y \leq 1$) single buffer layer on a sapphire substrate;

FIG. 3 is a schematic sectional view showing a $Ga_xAl_{1-x}N$ ($0 \leq x \leq 1$) crystal grown on a conventional GaN/GaN double buffer layers on a sapphire substrate;

FIG. 4 is a schematic sectional view showing a p-type GaN crystal grown on a periodic and alternating GaN/$Ga_xAl_{1-x}N$ ($0 \leq x \leq 1$) multi-layered buffer on a sapphire substrate according to Example 1 of the present invention;

FIG. 5 is a graph showing the relationship between the normalized photoluminescence (PL) intensity of the p-GaN (Mg doped) films and the number of the periods of alternating GaN/Ga$_x$Al$_{1-x}$N ($0 \leq x \leq 1$) in the multi-layered buffer according to Example 1 of the present invention. For the purpose of comparison, the results of the p-GaN films obtained according to the conventional growth methods, i.e., using a GaN or Ga$_y$Al$_{1-y}$N ($0 \leq y \leq 1$) single buffer layer, and GaN/Ga$_y$Al$_{1-y}$N ($0 \leq y \leq 1$) double buffer layers, are also shown in this figure;

FIG. 6 is a schematic sectional view showing a n-type GaN crystal grown on a periodic and alternating GaN/Ga$_x$In$_{1-x}$N ($0 \leq x \leq 1$) multi-layered buffer on a sapphire substrate according to Example 2 of the present invention;

FIG. 7 is a schematic sectional view showing a p-type Ga$_x$Al$_{1-x}$N ($0 \leq x \leq 1$) crystal grown on a nonperiodic multi-layered buffer consisting of alternating GaN/Ga$_y$Al$_{1-y}$N ($0 \leq y \leq 1$) in which each GaN or Ga$_y$Al$_{1-y}$N layer has different layer thickness on a sapphire substrate according to Example 3 of the present invention;

FIG. 8 is a schematic sectional view showing a n-type Ga$_x$Al$_{1-x}$N ($0 \leq x \leq 1$) crystal grown on a nonperiodic multi-layered buffer consisting of alternating GaN/Ga$_y$In$_{1-y}$N ($0 \leq y \leq 1$) in which each Ga$_y$In$_{1-y}$N layer has different y value, i.e. different Ga and In composition on a sapphire substrate according to Example 4 of the present invention.

DETAILED DESCRIPTION OF THE
PREFERRED EMBODIMENTS

According to the present invention, a periodic or nonperiodic multi-layered buffer in which the layers alternate between two types of compound semiconductors A and B different from each other in lattice constant and energy band gap, is grown on a sapphire substrate by means of MOCVD at a first (low) temperature before the growth of the group-III nitride or related compound semiconductors. Since the growth temperature for this multi-layer buffer layer is usually much lower than the temperature at which a nitride single crystal can be formed, the buffer layer is of an amorphous or polycrystalline state, as confirmed by our experiment and reported by other reseach groups over the world. In fact, this is just the reason why we name the buffer of the present invention as "multi-layered buffer" rather than "multi-quantum wells or superlattice buffer". Although the layered structure of the latter is somewhat similar to that of the former, following the definition,

multi-quantum wells and superlattice are strictly periodically formed monocrystalline whereas the multi-layered buffer of the present invention is amorphous or polyscrystalline and may not be formed periodically, i.e., each layer in the buffer can have a different layer thickness and/or composition.

As the temperature is raised to the second (high) temperature for the growth of the group-III nitride-based compound semiconductor crystals on the multi-layered buffer, the amorphous or polycrystalline buffer will partially change to monocrystalline due to the recrystallizing effect to serve as seed crystal. Compared with the conventional single or double buffer, the multi-layered buffer of the present invention demonstrates the ability to accommodate the strain arising from the lattice mismatch between the group-III nitride-based compound semiconductors and the sapphire substrate, and to form the seed crystal more effectively. According to the present invention, the crystalline quality of the group-III nitride-based compound semiconductors can be significantly enhanced by using the multi-layered buffer because the strain-accommodating and recrystallizing effects which are of crucial importance in improving the crystalline quality of the group-III nitride-based compound semiconductors, seemed to be more profound in the multi-layered buffer than in the single and double buffer layers. Moreover, since there is neither any limitation on selecting the constituent semiconductors of the multi-layered buffer, nor strict restriction on the layer thickness and the composition of each layer in the buffer, one can choose with great freedom the appropriate material combination to form the multi-layered buffer as convenient as possible for the subsequent growth of group-III nitride-based compound semiconductors on the formed multi-layered buffer. Note that although the multi-layered buffer of the present invention is amorphous (or polycrystal in some cases) and may not be formed periodically, i.e., each layer in the buffer can have different layer thickness and composition, there are of course optimal layer thickness and composition which depend on the constituent semiconductors and how they form the buffer (combination). A similar situation applies with respect to the growth conditions for the multi-layered buffer as well as the subsequently grown group-III nitrides and related compound semiconductors. However, in general, the preferred growth (said first or low) temperature for the buffer is within the range of (500-550 °C). On the other hand, the second or high growth temperature for the group-III nitride-based compound semiconductors is preferably 1,000 to 1,100 °C. Furthermore, in the case wherein the multi-layered buffer is formed periodically on a sapphire substrate, this buffer can be expressed by the formula

AB......AB. Here A and B represent one of two types of compound semiconductors different from each other in lattice constant and energy band gap.

In the present invention, the multi-layered buffer can be formed not only on a sapphire substrate but also on any substrate which are presently, already used or may be developed in the future, such as Si, SiC, GaP, InP, and GaAs substrates. It can even be formed on the surface of the epitaxial layers of the group-III nitrides and/or related compound semiconductors. This characteristic implies that the multi-layered buffer of the present invention can be applied to the regrowth of the group-III nitrides and/or related compound semiconductors.

Examples of the present invention will be described below with reference to the accompanying drawings. First, periodic and alternating GaN/Ga$_x$Al$_{1-x}$N ($0 \leq x \leq 1$) multi-layered buffer on a sapphire substrate (Example 1) which can overcome the drawbacks of conventional growth methods employing single or double buffers will be described in detail. Subsequently, several specific multi-layered buffers which are periodic or nonperiodic in layer thickness and composition (Examples 2 to 4) will be described. These examples, however, merely exemplify the method of practicing the technical concepts of the present invention. Therefore, the method of the present invention is not particularly limited to the following examples in terms of, for example, the growth conditions and the combination of the materials used. Various modifications can be made for the growth method of the present invention in accordance with the scope of claims.

Example 1

FIG. 4 shows a p-type GaN crystal grown on a periodic and alternating GaN/Ga$_x$Al$_{1-x}$N ($0 \leq x \leq 1$) multi-layered buffer on a sapphire substrate according to Example 1 of the present invention. Referring to FIG. 4, GaN and Ga$_x$Al$_{1-x}$N ($0 \leq x \leq 1$) thin films are periodically and alternately grown on a chemically cleaned sapphire substrate at a first (low) temperature of 525 °C. The film thickness of GaN and Ga$_x$Al$_{1-x}$N are set to 3 nm and 5 nm, respectively. The number of the GaN/Ga$_x$Al$_{1-x}$N repeated unit is changed from 3 to 12, corresponding to a total layer thickness of the multi-layered buffer varying from 24 nm to 96 nm. Subsequently, a 2 μm-thick Mg-doped p-type GaN epitaxial layer (monocrystalline) is grown on the surface of the formed multi-layered buffer at a second

(high) temperature of 1,050 °C. For comparison with the conventional methods using AlN (FIG. 1) and GaN (FIG. 2) single buffer, and GaN/GaN double buffers (FIG. 3), a single GaN buffer and a single $Ga_xAl_{1-x}N$ buffer with an identical layer thickness of 25 nm which is the optimal value reported so far in the case of single buffer layer, are stacked on sapphire substrates, respectively. In addition, the GaN/$Ga_yAl_{1-y}N$ $(0 \leq y \leq 1)$ double buffers in which each buffer has the same layer thickness of 10 nm and was deposited successively at two different temperatures of 600 and 500 °C were also grown on sapphire substrate in the same way as that reported by Uchida et al.

After the growth, a Hall effect measurement was performed at room temperature to determine the electronic properties, more specifically, the majority carrier concentration, the mobility, and the resistivity of the p-type GaN epitaxial layer. On the other hand, a photoluminescence (PL) measurement was carried out at room temperature in order to characterize the crystalline quality of the grown p-type GaN epitaxial layers and to compare the optical property, more specifically, the PL intensity of the p-type GaN samples grown by using the multi-layered buffer with those samples grown by means of the conventional buffers. According to the Hall measurement results, for example, the majority carrier concentration, the mobility, and the resistivity of the p-type GaN sample grown by using three periods GaN/$Ga_yAl_{1-y}N$ (y=0.1) multi-layered buffer, are 2.2 x 10^{17} cm^{-3}, 14.5 cm^2/Vsec., and 1.5 Ωcm, respectively. These values are slightly better than the corresponding results reported recently by Nakamura and Fasol ("The blue light laser diode", Springer, 1997) who used a single GaN buffer layer. On the other hand, the optical property, more specifically, the PL intensity of the p-type GaN samples grown by using the multi-layered buffer of the present invention was found to be much stronger than those samples grown by using conventional single or double buffers provided that the number of the periods of GaN/$Ga_xAl_{1-x}N$ $(0 \leq x \leq 1)$ in the multi-layered buffer is less than 6 or the total layer thickness of the multi-layered buffer is thinner than 48 nm.

FIG. 5 shows the relationship between the normalized PL intensity of the p-GaN (Mg doped) films and the number of the periods of alternating GaN/$Ga_xAl_{1-x}N$ $(0 \leq x \leq 1)$ in the multi-layered buffer according to Example 1 of the present invention. The results of the p-GaN films obtained according to the conventional growth methods, i.e., using a single GaN or $Ga_yAl_{1-y}N$ $(0 \leq y \leq 1)$, or GaN/$Ga_yAl_{1-y}N$ $(0 \leq y \leq 1)$ double buffer layers, are also shown in this figure. As is apparent from FIG. 5, the PL intensity of the p-type GaN

samples grown by using the multi-layered buffers are much stronger than those grown by using conventional methods provided that the number of the periods of $GaN/Ga_xAl_{1-x}N$ (0 $\leq x \leq$ 1) multi-layered buffer is less than 6 or the total layer thickness of the multi-layered buffer is thinner than 48 nm. This fact indicates that by using the multi-layered buffer, the crystalline quality of the group-III nitrides and related compound semiconductors can be significantly improved. Furthermore, most intense PL signal was detected from the p-type GaN sample in which a multi-layered buffer with three periods of $GaN/Ga_xAl_{1-x}N$ (0 $\leq x \leq$ 1) and a total layer thickness of 24 nm. This phenomenon implies that there should be optimal values for the number of periods of the $GaN/Ga_xAl_{1-x}N$ and the total layer thickness of the multi-layered buffer. These optimal values, of course, are strongly dependent on the layer thickness and the composition of each constituent layer, as well as the material combination selected for the multi-layered buffer.

Unfortunately at the present time there is no reliable theory in terms of which one can explain the physical mechanism of the multi-layered buffer and determine or predict the optimal layer thickness of the multi-layered buffer for a special material combination. In other words, the optimal value for a special material combination can now only be determined by experiment. However, the existence of the optimal layer thickness for the multi-layered buffer can be interpreted qualitatively as follows. Generally a buffer layer grown at a low temperature provides seed crystals which act as nucleation sites with low orientational fluctuation to promote the lateral growth of the group-III nitrides. A double buffer, especially a multi-layered buffer provide additional interfaces for the misfit dislocations to terminate. However, if the multi-layer buffer is too thin, it may neither effectively accommodate the elastic strain due to the large lattice mismatch between the group-III nitride crystals and the sapphire substrate nor provide sufficient amount of seed crystals for the subsequent growth of the group-III nitrides. On the other hand, if the multi-layered buffer is too thick, it tends to bring about excessive amount of the seed crystals with high orientational fluctuation. Therefore, there should be an optimal layer thickness for the multi-layered buffer. As shown in FIG. 5, the present inventors have experimentally found that most intense PL intensity can be obtained by using a multi-layered buffer with three periods of $GaN/Ga_xAl_{1-x}N$ (0 $\leq x \leq$ 1) and a total layer thickness of 24 nm which is near the optimized layer thickness for single and double buffer layers reported so far.

Example 2

FIG. 6 is a schematic sectional view showing a n-type GaN crystal grown on a periodic and alternating GaN/$Ga_xIn_{1-x}N$ ($0 \leq x \leq 1$) multi-layered buffer on a sapphire substrate according to Example 2 of the present invention. Referring to FIG. 6, GaN and $Ga_xIn_{1-x}N$ ($0 \leq x \leq 1$) thin films are periodically and alternately grown on a chemically cleaned sapphire substrate at a first (low) temperature of 525 °C. The film thickness of GaN and $Ga_xIn_{1-x}N$ are set to 3 nm and 5 nm, respectively. The number of the periods of the GaN/$Ga_xIn_{1-x}N$ is changed from 2 to 12, corresponding to a total layer thickness of the multi-layered buffer varying from 16 nm to 96 nm. After the growth of the multi-layered buffer, a 2 μm-thick Si-doped n-type GaN epitaxial layer (monocrystalline) is grown on the surface of the formed multi-layered buffer at a second (high) temperature of 1,050 °C.

Note that the multi-layered buffer in Example 1 consisted of GaN and $Ga_xAl_{1-x}N$, whereas GaN and $Ga_xIn_{1-x}N$ are used as the buffer here. Since the melting point of InN (1,100 °C) is much lower than that of GaN (1,700 °C) and AlN (3,000 °C), it is easy for the amorphous or polycrystalline GaN/$Ga_xIn_{1-x}N$ multi-layered buffer formed at low temperature to convert into monocrystalline as the temperature is raised to a high temperature. In other words, seed crystals with low orientational fluctuation can be obtained more easily by using the GaN/GaInN combination rather than by using the GaN/AlGaN combination. In addition, an improvement in the crystalline quality of GaInN can be expected when using such a GaN/GaInN multi-layered buffer, since the GaInN-based epitaxial layers are grown on the buffer layer consisting of similar material. This characteristic indicates that the multi-layer buffer of the present invention is of much greater flexibility in choosing the constituent materials of the buffer as compared with the conventional methods, which may play a crucial role in improving the crystalline quality of the group-III nitride-based compound semiconductors.

Example 3

FIG. 7 is a schematic sectional view showing a p-type $Ga_xAl_{1-x}N$ ($0 \leq x \leq 1$) crystal grown on an alternately formed but nonperiodic GaN/$Ga_yAl_{1-y}N$ ($0 \leq y \leq 1$) multi-layered buffer in which each GaN or $Ga_yAl_{1-y}N$ layer has different layer thickness on a sapphire substrate according to Example 3 of the present invention. Referring to FIG. 7, GaN and

$Ga_yAl_{1-y}N$ ($0 \leq y \leq 1$) thin films are alternately grown at a first (low) temperature of 525 °C.

but varying nonperiodically in layer thickness on a cleaned sapphire substrate. The film thicknesses of $GaN/Ga_yIn_{1-y}N$ are set to 2 and 4 nm, 3 and 5 nm, and 4 and 6 nm, respectively. The total layer thickness of the multi-layered buffer is hence 24 nm. After the growth of the multi-layered buffer, a 2 μm-thick Mg-doped p-type $Ga_xAl_{1-x}N$ ($0 \leq x \leq 1$) epitaxial layer (monocrystalline) is grown on the surface of the formed multi-layered buffer at a second (high) temperature of 1,050 °C.

Note that as compared with the Examples 1 and 2, the $GaN/Ga_yAl_{1-y}N$ ($0 \leq y \leq 1$) multi-layered buffer in this example is formed nonperiodically in layer thickness. This feature demonstrates that besides the great flexibility in choosing the constituent materials, the multi-layer buffer of the present invention can even be formed nonperiodically in layer thickness. In contrast, a superlattice or a quantum wells structure must be formed strictly periodically in layer thickness as well as the solid composition. This is another flexibility provided by the introduction of the multi-layered buffer and an important advantage over the conventional single or double buffer.

Example 4

FIG. 8 is a schematic sectional view showing a n-type $Ga_xAl_{1-x}N$ ($0 \leq x \leq 1$) crystal grown on a nonperiodic and alternating $GaN/Ga_yIn_{1-y}N$ ($0 \leq y \leq 1$) multi-layered buffer in which each $Ga_yIn_{1-y}N$ layer has different y value, i.e. different Ga and In composition on a sapphire substrate according to Example 4 of the present invention. Referring to FIG. 8, GaN and $Ga_yIn_{1-y}N$ ($0 \leq y \leq 1$) thin films are alternately grown at a first (low) temperature of 525 °C but nonperiodic in solid composition on a chemically cleaned sapphire substrate. The film thickness of GaN and $Ga_yIn_{1-y}N$ are set to 3 nm and 5 nm, respectively, and the number of the periods of the $GaN/Ga_yIn_{1-y}N$ is fixed at 3, corresponding to a total layer thickness of 24 nm. On the other hand, the In composition (1-y) for the $Ga_yIn_{1-y}N$ layers in sequence along the direction pointing from the sapphire substrate to the surface is, 0.10, 0.15, and 0.20, respectively. After the growth of the multi-layered buffer, a 2 μm-thick Si-doped n-type $Ga_xAl_{1-x}N$ ($0 \leq x \leq 1$) epitaxial layer (monocrystalline) is grown on the surface of the formed multi-layered buffer at a second (high) temperature of 1,050 °C.

As compared with the Examples 1-3, the GaN/$Ga_yIn_{1-y}N$ ($0 \leq y \leq 1$) multi-layered buffer in this example is formed periodically in layer thickness but nonperiodically varied in Ga and In composition through the buffer. This feature indicates that besides the flexibility in choosing the constituent materials and in the thickness for each layer, the multi-layer buffer of the present invention can also be formed nonperiodically in solid composition. This flexibility is only available for the multi-layered buffer but can never be realized by using the conventional single or double buffer.

Additional advantages and modifications will readily occur to those skilled in the art. Therefore, the invention in its broader aspects is not limited to the specific details, and representative devices, shown and described herein. Accordingly, various modifications may be made without departing from the spirit or scope of the general inventive concept as defined by the appended claims and their equivalents.